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Polyvinylidene fluoride/hydroxyapatite/ β -tricalcium phosphate multifunctional biocomposite: potentialities for bone tissue engineering

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ABSTRACT

Bioactive ferroelectric composites based on polyvinylidene fluoride, hydroxyapatite and β -tricalcium phosphate have been synthesized and their structural, microstructural, bioactive, and ferroelectric properties are characterized. Structural and FTIR investigations showed the presence of the polar polyvinylidene fluoride (β_2) phase, while ferroelectric characterizations revealed remnant polarizations and coercive field, around $0.04 \mu\text{C}/\text{cm}^2$ and $28 \text{ kV}/\text{cm}$, respectively, for these biocompatible samples. Structural and microstructural analysis of samples previously immersed in simulated body fluid for 7 days revealed a large apatite phase growth ($1.45 \mu\text{m}$) on the composites' surfaces as a strong indication of their elevated bioactivity and potentialities for bone tissue engineering.

1. Introduction

The search for innovative and advanced materials for biological applications has been intensified in the recent years. This is because the advances in modern medicine, especially in the orthopedic and traumatology, are directly linked to the specific properties of these materials and new techniques for their synthesis and characterization [1]. However, for satisfying the expectations of future advanced medicine protocols it is necessary to obtain revolutionary materials, which may indicate new directions and provide faster results than those currently available. In this sense, novel multifunctional materials have emerged as strong candidates to fulfill some gaps to the biomedical applications. This is the basis for studying (ferro)piezoelectric/bioactive compounds, which can catalyze the bone growth by piezoelectric voltage and/or electro-mechanical extension/contraction stimuli [2]. In fact, piezoelectric effect has been studied not only as catalyst, but also, as a possible mechanism for bone growth [2,3]. Figure 1 shows a schematic picture of a possible novel technique to accelerate the bone growth. In this schematic, a (ferro)piezoelectric/bioactive composite/compound is implanted in a specific region of a damaged bone and an alternating external electric field, which can also be overlapped by a bias electric field, is applied. The converse piezoelectric effect tunes the vibration of the implant (alternated mechanical deformation, contraction/extension movement), rearranging the electric charges on implant surfaces (reversing the negative and positive electric poles in the surface regions), stimulating bone tissue growth by ion exchange (inset - Fig. 1) and accelerating the healing process. This technique produce better results in the healing process in orthopedics areas, because it has been shown that the mechanisms of osseous growth are based on ionic exchanges [1].

Usually, bioactive calcium phosphates, such as the hydroxyapatite (HAp – $\text{Ca}_5(\text{PO}_4)_3\text{OH}$), allows an elevated usability in medicine and dentistry, notably in bone implants and reconstruction and/or replacement of bone tissues. In fact, the HAp use has grown constantly due to the improved quality of life provided by its application in partial or full replacement of fractured bones.

Furthermore, HAp ceramics tend to present special characteristics that are very similar to those of the animal bone, as osteoconduction that is the process by which bone growth takes place on a surface [4,5]. Indeed, these characteristics have been associated to the similar structure and chemical bonds usually found in mineral bone matrices and HAp [6]. In tissue engineering, other widely studied calcium phosphate compound for bone replacements is the β -tricalcium phosphate (β -TCP – $\text{Ca}_3(\text{PO}_4)_2$). This phosphate is a resorbable material and has the properties of bioactivity, nontoxicity, and osteoconductivity, so there is no need of a second surgical procedure to remove an implant composed by β -TCP after bone healing process [7]. Several authors have verified that biphasic ceramics of HAp and β -TCP (namely, HA β) can be more advantageous in terms of bioactivity than HAp or β -TCP alone [8,9]. The HA β concept is determined by the optimum balance between a more stable HAp and a more soluble β -TCP phase.

In this context, some alternative polymer/ceramic composites have been tested for bioactive applications [1-5]. Also, polymeric composites can be used to bone reconstruction, being molded into any shape (machining), sintered at low temperatures and developed as a tissue (electrospun, for example). Besides that, polymeric composites can be tailored to show thermal properties more similar to the bone than metallic materials. Furthermore, their use is justified mainly due to their elevated biocompatibility, reasonable mechanical properties and in some cases, multifunctional properties that can be used simultaneously to increase the healing process. Recently, Hench [10] has shown that the stress/strain ratio of the polymer/ceramic composite can be adjusted closer to the bone than that of the individual phases. Controversially, recent studies on $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ /polyethylene [11] and HAp/Poly(lactic acid) (PLLA) [12,13] composites revealed their inadequate mechanical properties for bone replacement. Considering electrically active composites, and mainly those that show piezoelectric response (as the β_2 -polar phase of the polyvinylidene fluoride (PVDF) polymer [14]), there is a potential for this class of materials to be used in techniques leading to accelerate those processes involved in the healing, as indicated in Fig. 1. Considering biomedical applications, PVDF-based composites are usually bioactive and non-toxic,

and have been successfully applied in the construction of hernia meshes and bone tissue healing [15]. The converse piezoelectric effect of PVDF may also be used to effectively stimulate bone growth at the bone implant interface. Braga et al. [16] showed that it is possible to incorporate an amount of hydroxyapatite into the PVDF matrix in a film form, forming a satisfactorily homogeneous composite with potential to medical and dental applications. Interesting contributions, indicating the high potential of the PVDF polymer for tissue engineering have been reported in the last years [17-21]. In fact, a high proliferation of osteoblasts cells was observed in experiments of cell culture in PVDF films, with an even high proliferation of osteoblast cells in polar PVDF (β -PVDF) than in non-polar (α -PVDF) one [17]. A high bioactivity of poled PVDF films, in comparison with non-poled ones, was identified [18], and an elevated adhesion/proliferation of osteoblast cells was obtained under mechanical stimulation [19]. Furthermore, different types of tissue engineering applications have been reported for the PVDF polymer, as the synthesis of Scaffold [20] and the use of Electrospray [21]. Thus, in search of a piezoelectric/ferroelectric material for the production of multifunctional bioactive composite, PVDF polymer appears to be a good alternative, since the commercial materials with high piezoelectric activity, such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), contain Lead, which is toxic to the human body. Considering all these facts, in this work promising bioactive Polyvinylidene Fluoride/Hydroxyapatite/ β -tricalcium phosphate (PVDF-HA β) composites were synthesized in bulk form and their structural, microstructural, chemical and bioactivity properties were analyzed. The results reveal that the polar PVDF β_2 -phase increased in the composite, increasing its (ferro)piezoelectric activity. The bioactive tests also pointed out that these composites have potentials to be used for the bone replacement.

2. Materials and Methods

2.1 Materials

HA β powders, a composite of hydroxyapatite (HAp – Ca₅(PO₄)₃OH) and β -tricalcium phosphate (β -TCP – Ca₃(PO₄)₂) phases, were obtained from calcined fish bone, as previously reported [22,23]. The bones were calcined in air atmosphere at 900 °C for 8 h, then crushed inside an agate crucible and submitted to high-energy milling for 8h with rotational speed of 300 rpm in order to create the precursor material used in this study. The milling process was performed in a Retsch PM100 planetary ball mill, using vial and balls (10 mm of diameter) of yttria-stabilized zirconia in a ball/mass ratio of 6:1. Polyvinylidene fluoride (PVDF) commercial powders (99.8% of purity) were purchased from Alfa Aesar.

2.2 Method

HA β and PVDF powders were mixed in an agate mortar in a ratio PVDF:HA β of 9:1 (vol%) for 1 h, forming the (0.9)PVDF-(0.1)HA β composite (PVDF-HA β). This composite was compacted (by uniaxial pressing) at 450 MPa in disc forms with approximately 1 mm of thickness and 10 mm of diameter. The conformed composites were heat-treated at 170 °C for 1 h in air (consolidation process). Before the *in-vitro* bioactivity tests, the consolidated pellets were sanded with a 400# silicon carbide paper, rinsed in an ultrasonic cleaner with distilled water, ethanol and deionized water, and then dried in air at 40 °C. Simulated body fluid (SBF), which simulates the conditions of human body for preliminary bioactivity tests (*in-vitro* tests) [24] was used to investigate the PVDF-HA β bioactivity. This technique, developed and extensively tested by Kokubo and Takadama [25] permits evaluating the calcium phosphate (apatite) forming ability on the surface of biomaterials when immersed in SBF (by simulating a growing medium similar to that of the human body). PVDF-HA β samples were then immersed in polypropylene tubes with SBF that were maintained for 7 days in a water bath at 36.5 °C. After immersion, the samples were removed from the solution, washed with deionized water, dried in air at 40 °C and submitted to the physical characterizations.

2.3. Physical Characterization

Room temperature structural characterizations were performed by X-ray diffraction (XRD) using a SHIMADZU XRD7000-diffractometer (Cu K_{α} radiation, $\lambda = 1.541 \text{ \AA}$). The samples were scanned over a range of 2θ from 10° to 60° at a scanning rate of $1^{\circ} (2\theta)/\text{min}$. To test the samples surface, the equipment was set-up in the θ - θ configuration to perform the grazing incident angle protocol, where the incident angle is fixed at 1° and the X-ray detector perform a scan over a range of θ from 10° to 60° at a scanning rate of $1^{\circ} (2\theta)/\text{min}$. To investigate samples morphology, as well also to verify apatite-forming on samples' surface, scanning electron microscopy (SEM) was performed with a SHIMADZU SS550 SuperScan microscope by using secondary electrons detection. Functional groups in the raw materials and processed composites were investigated by Fourier transform infrared spectroscopy (FTIR), performed in a Bruker Vetex 70 V spectrometer, in the transmission mode, by using KBr pellets in the range of $4000 - 400 \text{ cm}^{-1}$ (4 cm^{-1} of resolution). The ferroelectric response of the processed composites was investigated by obtaining ferroelectric hysteresis loops in a homemade Sawyer-Tower circuit, as previously reported [26].

3. Results

3.1 Composite Preparation

HA β (HAp + β -TCP) and PVDF powders were stoichiometrically mixed to form (0.9)PVDF-(0.1)HA β composite (PVDF-HA β). This specific composition was designed to maximize the ferroelectric/piezoelectric response of the polymeric PVDF matrix, ensuring the composite bioactivity. The PVDF-HA β composite indeed showed microstructural characteristics (see section 3.2) that indicates the feasibility of the experimental protocol used in this work to

process this kind of sample. The consolidated composites were immersed in the SBF solution to verify the bone-like apatite formation on their surfaces.

3.2 Structural Study

The XRD results for HA β and PVDF precursors, and for PVDF-HA β composites before and after immersion in SBF for 7 days (henceforth PVDF-HA β 7) are shown in Fig. 2. The XRD patterns obtained for the HA β (Fig. 2(a)) sample were indexed with a major ($P6_3/m$ space group, HAp phase, H index in Fig. 2(a)) and a secondary ($R3c$ space group, β -TCP phase, β index) hexagonal phases, as expected. Fig. 2(b) shows the conventional diffraction pattern for the consolidated PVDF polymer, which was indexed with a major monoclinic phase (nonpolar α -phase, $P21/c$ space group) along with a secondary piezoelectrically active orthorhombic phase (β_2 = PVDF polar β -phase, $Cm2m$ space group). The XRD patterns for PVDF-HA β composites before and after 7 days of immersion in SBF are shown in Figs. 2(c) and (d), respectively. Both XRD show overlapped patterns derived from the PVDF polymer and the HA β ceramic. Curiously, when comparing the two diffraction patterns it is seen an increase of some peaks intensity (labeled as H+A) of the composite after immersion in SBF (Fig. 2(d)). This increase can be related to the growth of an apatite layer on sample surface [27]. In order to keep the structural investigations focused to the apatite layer on PVDF-HA β 7 surface, XRD experiments in a grazing incident angle configuration were performed on this sample, as shown in Fig. 2 (insets (i), (ii), and (iii)). In this experiment, illustrated out of scale in Fig. 2 - inset (i), the X-ray beam penetrates $\sim 30\text{ }\mu\text{m}$ in the sample in a grazing incident angle ($\theta = 1^\circ$). Thus, by using the triangle geometry, it is easy to obtain the vertical depth of beam penetration in the sample, i. e., $y \sim 0.5\text{ }\mu\text{m}$. As the grown apatite layer is well-adhered and has around $1.45\text{ }\mu\text{m}$ of thickness and a globular nucleation morphology (see Figs. 3(c) and (d), SEM analysis), it is possible to extract that only the upper layer of the grown apatite is actually tested in this experiment. In this way, by using this protocol an XRD pattern similar to that

of PVDF was collected on the surface of the PVDF-HA β composite before immersion in SBF (Fig. 2 – inset(ii)). On the other hand, the XRD pattern collected on the surface of the PVDF-HA β 7 sample (Fig. 2 – inset(iii)) was better indexed to an apatite structure of low crystallinity, unambiguously proving the apatite growth promoted by the interaction among the PVDF-HA β 7 sample surface and the SBF medium, as well as the high bioactivity of this composite.

3.3. Microstructural and Morphological Study

Figure 3 shows the SEM images obtained for PVDF, PVDF-HA β and PVDF-HA β 7 samples. The fracture images reveal very few differences in the morphology of PVDF (Fig. 3(a)) and PVDF-HA β composite (Fig. 3(b)) before immersion in SBF. In fact, HA β concentration is small in the composite (10% of the volume fraction). In this way, major microstructural changes are not expected. On the other hand, when the composite is immersed in SBF for seven days its surface (Fig. 3(c)) and fractured surface (Fig. 3(d)) completely changed. A new morphology and microstructure emerge due to the globular nucleation of an apatite layer composed of agglomerated nanometric grains. In fact, in the fracture image (Fig. 3(d)) a large apatite layer ($\sim 1.45 \mu\text{m}$) is observed, while the profile surface image (Fig. 3(c)) shows apatite globules around $3.30 \mu\text{m}$ in diameter.

3.4. FTIR Investigations

Figure 4(a) shows the FTIR absorption spectrum for the PVDF sample, evidencing the characteristic bands of α , β_2 and γ phases of PVDF polymer. The bands observed at 613, 764, 978, and 1184 cm^{-1} , and the shoulders at 534 and 795 cm^{-1} , correspond to the normal modes of the α phase [14,28,29]. The bands at 1280, 1076 and 510 cm^{-1} are related to the β_2 phase [28], and the bands at 947 and 1116 cm^{-1} are related to the γ phase [30,31]. There are three regions of overlapped

bands related to more than one phase. The regions nearby 1404 cm^{-1} are assigned to α , β_2 and γ phases, and the bands at 840 and 883 cm^{-1} could be associated to β_2 and/or γ phases [28]. The bands at 1452 and 678 cm^{-1} are assigned to polymer chain defects (*) associated to head-to-head and tail-to-tail linkages. The broad band between 1560 and 1690 cm^{-1} could be related to vibrations C=C stretching [30] and/or adsorbed water (H-O-H bending) [32]. In the large band in the region between 3600 and 3100 cm^{-1} the presence of adsorbed water is also noted [33]. Figure 4(b) shows the characteristic bands of phosphate group (PO_4^{3-}) and hydroxyl (OH^-) of HAp and of β -TCP. The vibrations occur at 569 and 602 cm^{-1} are due to the bending vibrations (O-P-O) that are vibration modes triply degenerated (ν_4) of HAp. The band at 962 cm^{-1} corresponds to the non-degenerated symmetrical stretching mode (ν_1) of the P – O bond of this phase. The bands at 1045 and 1091 cm^{-1} represent the asymmetric stretching modes with triple degeneracy (ν_3) of the P-O bonds [34]. The OH^- vibrations (ν_L) at 632 cm^{-1} and (ν_S) at 3571 cm^{-1} correspond to the OH bond in $\text{HA}\beta$ structure [35]. The weak bands at 947 , 985 and 1122 cm^{-1} are associated to the presence of the secondary β -TCP phase in $\text{HA}\beta$ [35]. The absorbance spectrum of the PVDF- $\text{HA}\beta$ composite (Fig. 4(c)) shows the same bands of pure $\text{HA}\beta$ and PVDF samples. As can be seen, the vibration modes of $\text{HA}\beta$ are more intense in FTIR than those of PVDF. Fig. 4(d) shows the characteristic FTIR spectrum of the bone-like apatite grown on the PVDF- $\text{HA}\beta$ 7 surface. By comparing this spectrum with that of $\text{HA}\beta$ (Fig. 4(b)), the presence of additional bands around 870 cm^{-1} , and a broad band between 1375 and 1555 cm^{-1} could be related to carbonate ions (CO_3^{2-}) [33]. On the other hand, the band at 1640 cm^{-1} and the large band between 3600 and 3100 cm^{-1} are assigned to the O-H vibrations of the H_2O that was adsorbed on the apatite layer [33,35]. It is worth noting that the bands in the apatite layer (Fig. 4(d)) are broader than those of raw $\text{HA}\beta$.

3.5. Ferroelectric Study

The ferroelectric behavior of the PVDF-HA β sample was revealed by its ferroelectric hysteresis loop (at room temperature and 30 Hz), as shown in the Fig. 5. The composite prepared with the PVDF matrix shows high electric resistivity sustained an elevated external electric field (~ 60 kV/cm). The ferroelectric behavior was evidenced by the typical ferroelectric remnant (~ 0.04 $\mu\text{C}/\text{cm}^2$) and saturation (~ 0.1 $\mu\text{C}/\text{cm}^2$) polarizations. Furthermore, the PVDF-HA β sample showed a coercive ferroelectric field of ~ 28 kV/cm at room temperature. The unsaturated ferroelectric hysteresis loop of the PVDF-HA β composite indicates a possible time-dependent behavior, as experienced and indicated by simulations reported in the literature [36]. Of course, other methods of synthesis may be easily employed in order to maximize the ferroelectric PVDF responses in the PVDF-HA β composite, as shown in literature [17-21]. In this way, the exploiting of the multifunctionalities of the PVDF-HA β composites, as bioactivity, ferroelectricity and piezoelectricity, can be enhanced as compared to the obtained results.

4. Discussion

XRD analyses revealed that in the synthesized composites the polar β_2 -phase amount increased due to the consolidation process. This fact is very interesting considering the potential applications as illustrated in Fig. 1 (electric field induced bone growth), provided the piezoelectric polar β_2 -phase can be used for this purpose [18]. The XRD patterns obtained by grazing incident angle, showed in insets (ii) and (iii), allowed observing only the diffraction patterns referring to the samples' surface. Thus, comparing the XRD patterns of the composite before and after SBF immersion, one can directly see an apatite layer emerging on the PVDF-HA β 7 surface by the occurrence of the A diffraction peaks. In fact, the XRD pattern obtained on PVDF-HA β surface before immersion in SBF (Fig. 2(d) - Inset (ii)) is characteristic of the PVDF polymer, which is expected for the composite with low concentration of HA β . The XRD pattern obtained on PVDF-HA β 7 surface (Fig. 2(d) - Inset (iii)) reveals an apatite layer of low crystallinity, which is expected

in the upper layers of the grown apatite. These results clearly indicated that the PVDF-HA β composite is strongly bioactive and reveal its great potential for biological applications where bone growth and bone tissues replacement are the target.

The microstructural study in surfaces of the analyzed samples revealed very few differences between the morphologies of PVDF (Fig. 3(a)) and PVDF-HA β composite (Fig. 3(b)) before immersion in SBF. This behavior is notably due to the small HA β concentration in the composite (10% of the volume fraction). The major microstructural changes were only observed when the composite was immersed in SBF for seven days. In this case, its profile (Fig. 3(c)) and fractured (Fig. 3(d)) surfaces completely changed, and a new morphology and microstructure emerged due to the globular nucleation of an apatite layer composed by agglomerated nanometric apatite grains. A thicker apatite layer ($\sim 1.45 \mu\text{m}$) and apatite globules ($\sim 3.30 \mu\text{m}$ in diameter) were observed in this sample. These results unambiguously proved the large bioactivity of the PVDF-HA β composite and highlighted the large growing ratio of apatite on the composites surface.

The FTIR study revealed the presence of the three structurally distinct α , β_2 (polar PVDF β -phase) and γ phases in PVDF raw material. Furthermore, considering the HA β analysis, characteristic bands of phosphate group (PO_4^{3-}) of HAp and hydroxyl (OH^-) of β -TCP were observed and the absorbance spectrum of the PVDF-HA β composite (Fig. 4(c)) showed the same bands of pure HA β and PVDF. However, and as seen in Fig. 4(c), the vibration modes of HA β appeared to be more intense in PVDF-HA β composite, but those vibrations associated to the polar β_2 -phase also can be seen in the PVDF-HA β before SBF immersion. These results corroborate the XRD ones (Figs. 2(c) and (d)) and reveal the intimate synergy between PVDF and HA β materials. In fact, the interaction between these phases during the consolidation process does not prevent the formation of the polar β_2 -phase of the PVDF polymer, which is very important for the designed applications. The characteristic FTIR spectrum of the apatite phase grown on the PVDF-HA β 7 surface (Fig. 4(d)) showed the presence of additional bands (at 870 cm^{-1} and a broad band between 1375 and 1555 cm^{-1}) related to carbonate ions (CO_3^{2-}) [33]. Interestingly, these vibrations are

commonly found in apatite grown by immersion in SBF, and their presence is attributed to the B-type substitution (PO_4^{3-} by CO_3^{2-}) in apatite structure, while the absence of the vibrational bands at 632 and 3571 cm^{-1} indicates an A-type substitution (OH^- by CO_3^{2-}) [37,38]. It is worth noting that the bands in the apatite layer (Fig. 4(d)) are broader than those of raw HA β . This behavior is associated to the low crystallinity of the precipitated layer. The crystallinity index (CI) for the three studied PO_4^{3-} -containing samples (Figs. 4(a), (b) and (c)) were determined by a semi-quantitative method proposed by Weiner and Bar-Yosef [39]. After a baseline correction, between 495 and 750 cm^{-1} , the sum of the PO_4^{3-} vibration bands intensities (at 602 and 569 cm^{-1}) was divided by the intensity of the valley between these absorption bands (above the baseline). These results are shown in Fig. 4 (inset). For HA β the CI was 6.13, while for the PVDF-HA β composite it was 5.33. This small difference can be associated with an interaction between PVDF and HA β that decreases its crystallinity, or simply to the fact of the overlapped PVDF and HA β bands in the region between 750 to 450 cm^{-1} shields the HA β response. For apatite grown in the SBF medium (Fig. 2, inset (iii)), the CI was about 2.5 times lower than HA β , indicating a low crystallinity which is similar to that of natural bone [40,41].

Analyzing the ferroelectric response/character (Fig. 5 - ferroelectric hysteresis loop) of the PVDF-HA β sample it was seen that this composite sustained an elevated external electric field (~ 60 kV/cm) and showed a small remnant polarization of 0.04 $\mu\text{C}/\text{cm}^2$ and an elevated coercive ferroelectric field of ~ 28 kV/cm at room temperature. This behavior is very similar to that reported for uniaxially stretched and post-annealed PVDF samples with different contents of the polar $\beta 2$ -phase [42]. In this way, it can be concluded that the retaining of the $\beta 2$ -phase in the polymeric matrix of the PVDF-HA β samples contributes to consolidate the ferroelectric response of the processed composites. Anyway, it is easily possible to improve, if desirable, the ferroelectric responses of the PVDF polymer and, consequently, of the PVDF-HA β composite with alternative synthesis routes and reach higher ferroelectric polarizations. Besides, other protocols can be used to further improve the composite bioactive response, such as electromechanical (dynamic) stimuli

using an ultrasound device and/or working with polarized samples, as indicated in the literature [18,**Error! Bookmark not defined.**]. So far, no upper safe limits of higher polarization and/or electrical conductivity have been set or reported.

In summary, the potentialities of the PVDF-HA β composites for biological applications were pointed out and discussed. The emergence of a thick apatite layer ($\sim 1.45 \mu\text{m}$) on the sample surface after few days (7 days) of immersion in SBF unambiguously proved the extremely high bioactivity of this composite. In consequence, the PVDF-HA β composite thus become a strong candidate for the multifunctional applications where, for example, it is possible to use external electric stimuli as a catalyst for bioactivity by exploiting its piezoelectric properties. In this way, the exploiting of the multifunctionalities of the PVDF-HA β composites, as bioactivity, ferroelectricity and piezoelectricity, can be envisaged on the light of the obtained results. The ferroelectric/piezoelectric active role, as an electrical stimulator, can be tailored to the specific needs.

5. Conclusions

In this manuscript, innovative and highly bioactive and tunable polymer/ceramic composites (PVDF-HA β) were synthesized and the first full set of characterizations were conducted. The analyses by XRD and SEM, conducted on PVDF-HA β composites with 0 and 7 day of immersion in SBF, reveal a high-bioactivity for the last one, which makes it promising for applications such as bone replacement. Furthermore, the infrared spectroscopy and XRD analysis showed that the high piezoelectric structure (β_2 – phase) from PVDF polymer is retained in the PVDF-HA β composite. The piezoelectric β_2 – phase, associated with remnant polarization of the ferroelectric hysteresis loop, introduces new possibilities for practical applications using multifunctional properties of the PVDF-HA β composite, such as the electric field as a catalyst for the bone growth process.

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FIGURE CAPTIONS

Fig. 1. Schematic (ferro)piezoelectric bioactive osseous implant activated/stimulated by static or oscillatory electric fields. Schematic (ferro)piezoelectric implant (Red (online) or light gray), ferroelectric dipole vectors (Blue (online) or dark gray) and double directional arrows shake (Blue (online) or dark gray) shaking under an external electric field.

Fig. 2. X-ray diffraction patterns for (a) biphasic hydroxyapatite - β -Tricalcium phosphate (HA β) ceramic, (b) consolidate polyvinylidene fluoride (PVDF), (c) (0.9)PVDF-(0.1)HA β composite (PVDF-HA β), and (d) (0.9)PVDF-(0.1)HA β composite (PVDF-HA β 7) after 7 days of immersion in simulated body fluid (SBF). Indexes: H = hydroxyapatite, β = β -tricalcium phosphate (β -TCP), β_2 = PVDF polar β -phase, α = PVDF α -phase, A = bone like apatite of low crystallinity. Insets: (i) Schematic diagram of the X-ray experiment with grazing angle. X-ray diffraction incident grazing angle ($\theta = 1^\circ$) analysis for (ii) PVDF-HA β and (iii) PVDF-HA β 7 samples

Fig. 3. Scanning electron microscopy images for (a) PVDF (fracture), (b) PVDF-HA β (fracture), (c) PVDF-HA β 7 (surface), and (d) PVDF-HA β 7 (fracture) samples.

Fig. 4. FTIR spectroscopy analysis for (a) PVDF, (b) HA β , (c) PVDF-HA β composite, and (d) apatite formed on the (PVDF-HA β) composite surface after 7 days immersed in simulated body fluid (PVDF-HA β 7 sample). (*) = polymer chain defects

Fig. 5. Ferroelectric hysteresis loop for the PVDF-HA β composite, at 300 K and 30 Hz.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Schematic (ferro)piezoelectric bioactive osseous implant activated/stimulated by static or oscillatory electric fields. Ferroelectric dipole vectors (red arrows) and reversible ferroelectric dipoles (blue double directional arrows) shaking under external oscillatory electric fields.